

Heavy Metals in Contaminated Soil: Sources & Washing through Chemical Extractants

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Abstract

Heavy metals that are commonly contaminating soil throughout the world include lead, chromium, arsenic, zinc, cadmium, copper, mercury and nickel. The main sources of these metals are dust produced by energy, transport, metallurgy, production of construction materials; sanitary sewage, chemical wastewater, industrial mining wastewater and urban mining mixed sewage; mining and industrial solid waste contamination; Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production. Among effective ways of removing heavy metals from soil, using chemical extractants are the most cost effective and less damaging, including organic acids and chelating agents.

Keywords: heavy metals; soil; contamination; chemical extractants.

1. Introduction

The mobility and toxicity of heavy metals are controlled by the interactions between metal ions and soil surfaces. Low concentrations of some metals such as Cu, Ni, and Zn, which strongly interact with soil components, may result in nutrient deficiency for living systems. Due to a large human population growth, soils have been subject to increasing sources of metal contamination. Atmospheric deposition, waste disposal, fertilizer and pesticide applications, industrial waste, and nuclear waste are some of the sources of heavy metals. Obviously, these sources can cause metal accumulation in soils. The excessive amounts of heavy metals introduced into the soils can affect soil matrices particularly involving metal-soil interactions, which further affect metal transport. At the interfaces of soils and soil solutions, various competitive reactions occur [1, 2].

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Heavy metal contamination of soil is one of the most important environmental problems throughout the world [3]. The ability of heavy metals to accumulate and cause toxicity in biological systems - humans, animals, microorganisms and plants has been reported [4].

Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) [5].

Remediation methods of contaminated soils with heavy metals can be roughly classified into physical or chemical, and phytoremediation [6]. Remediation mechanisms basically consist of two fundamental principles. The first is to completely remove contaminations from polluted sites and the second is to transform these pollutants to harmless forms by using one or more engineering technologies, which mainly include excavation, separation, extraction, electrokinesis, washing, oxidation, reduction, phytoextraction, phytovolatilization, or solidification, vitrification, among others [6-9].

Soil washing is particularly frequently used in soil remediation because it: (i) completely removes the contaminants, hence ensures the rapid cleanup of a contaminated site [10], (ii) meets specific criteria, (iii) reduces or eliminates long-term liability, (iv) may be the most cost-effective solution and (v) may produce recyclable material or energy [11].

Since heavy metals are sparingly soluble and occur predominantly in a sorbed state, washing the soils with water alone is expected to remove too low an amount of cations in the leachates, chemical agents have to be added to the washing water [12, 13].

1.2. Sources of heavy metals in contaminated soil

Excess heavy metals in the soil originate from many sources, which include atmospheric deposition, sewage irrigation, improper stacking of the industrial solid waste, mining activities, the use of pesticides and fertilizers [14], etc.

1.2.1 Atmosphere to soils pathway

Heavy metals in the atmosphere are mainly from gas and dust produced by energy, transport, metallurgy and production of construction materials. Excepting mercury, heavy metals basically go into the atmosphere in the form of aerosol and deposit to the soil through natural sedimentation and precipitation, etc. For example, the lead pollution [15] in a downtown, Central Sweden, was reported mainly from the urban industrial copper plant, sulfuric acid plant, paint factory, and the large amount of waste from mining and chemical industries. Due to transporting by wind, these fine lead particles spread from industrial waste heap to surrounding areas. The superimposed chromium contamination by a heavy industrial factory producing chromium [16] in Nanjing, was reported more than 4.4 times of the local background value. The chromium contamination was centered on the chimney of workshop, ranging up to 1.5 km², and extending 1.38 km away. A sulfuric acid production plant in Russia [17] was reported to contaminate the environment because of the discharge of S, V, and As from the

factory chimneys. Transport, especially the automotive transport, causes serious heavy metal contamination (Pb, Zn, Cd, Cr, Cu, etc.) of the atmosphere and soils [18].

1.2.2 Sewage to soils pathway

Wastewater can be divided into several categories, sanitary sewage, chemical wastewater, industrial mining wastewater and urban mining mixed sewage, etc. Heavy metals are brought to the soil by irrigative sewage and are fixed in the soil in different ways. It causes heavy metals (Hg, Cd, Pb, Cr, etc.) to continually accumulate in the soil year by year. Sewage irrigation is a feasible way to solve the problem of crop irrigation in the arid area. However, heavy metal contamination caused by sewage irrigation must be paid enough attention. Quality of irrigative sewage must be strictly controlled within the national quality standard for irrigation water [19].

1.2.3 Solid wastes to soils pathway

There are a variety of solid wastes which have complex composition. Of which mining and industrial solid waste contamination is the most serious. When these wastes are in the process of being piled or governed, heavy metals move easily due to the facilitation of sunlight, raining and washing. And they spread to the surrounding water and soils at the shape of funnel and radiation.

With the development of industry and the acceleration of urban environmental construction, sewage treatment is continuing to be strengthened. China now has more than 80 sewage treatment plants, with the estimated 400 million tons of sludge production. Due to the high content of organic matter, nitrogen and phosphorus in the sludge, soils become the main places for soil sludge treatment. In general, Cr, Pb, Cu, Zn and As in the sludge will exceed the control standards easily [19]. Solid wastes can expand contamination scope easily with the help of wind and water.

1.2.4 Agricultural supplies to soils pathway

Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production [20]. Nevertheless, the long-term excessive application has resulted in the heavy metal contamination of soils. The vast majority of pesticides are organic compounds, and a few are organic-inorganic compound or pure mineral, and some pesticides contain Hg, As, Cu, Zn and other heavy metals [21]. Heavy metals are the most reported pollutants in fertilizers. Heavy metal content is relatively low in nitrogen and potash fertilizers, while phosphoric fertilizers usually contain considerable toxic heavy metals. Heavy metals in the compound fertilizers are mainly from master materials and manufacturing processes. The content of heavy metals in fertilizers is generally as follows: phosphoric fertilizer > compound fertilizer > potash fertilizer > nitrogen fertilizer [22]. Cd is an important heavy metal contaminant in the soil. Cd is brought to soils with the application of phosphoric fertilizers. Many studies showed that, with the application of a large amount of phosphate fertilizers and compound fertilizers, the available content of Cd in soils increases constantly, and Cd taken by plants increases accordingly. In recent years, the mulch has been promoted and used in large areas, which results in white pollution of soils, because the heat stabilizers, which contain Cd and Pb, are always added in the production process of mulch. This increases heavy metal contamination of soils [23].

2. Effective Chemical Extractants for Soil Washing

For heavy metal-contaminated soils, the physical and chemical form of the heavy metal contaminant in soil strongly influences the selection of the appropriate remediation treatment approach. Information about the physical characteristics of the site and the type and level of contamination at the site must be obtained to enable accurate assessment of site contamination and remedial alternatives. The contamination in the soil should be characterized to establish the type, amount, and distribution of heavy metals in the soil. Once the site has been characterized, the desired level of each metal in soil must be determined. This is done by comparison of observed heavy metal concentrations with soil quality standards for a particular regulatory domain, or by performance of a site-specific risk assessment. Remediation goals for heavy metals may be set as total metal concentration or as leachable metal in soil, or as some combination of these [24, 25].

Generally remediation technologies for heavy metal-contaminated soils under five categories of general approaches to remediation: isolation, immobilization, toxicity reduction, physical separation, and extraction [26].

For less damaging washes, organic acids and chelating agents are often suggested as alternatives to straight mineral acid use [27]. Natural, low-molecular-weight organic acids (LMWOAs) including oxalic, citric, formic, acetic, malic, succinic, malonic, maleic, lactic, aconitic, and fumaric acids are natural products of root exudates, microbial secretions, and plant and animal residue decomposition in soils [28]. Thus metal dissolution by organic acids is likely to be more representative of a mobile metal fraction that is available to biota [29]. The chelating organic acids are able to dislodge the exchangeable, carbonate, and reducible fractions of heavy metals by washing procedures [30].

Many chelating compounds including citric acid [28], tartaric acid [31], and EDTA [30, 32, 33] for mobilizing heavy metals have been evaluated. The use of soil washing to remediate contaminated fine-grained soils that contained more than 30% fines fraction has been reported by several workers [34–36]. Khodadoust and his coworkers [37, 38] have also studied the removal of various metals (Pb, Ni, and Zn) from field and clay (kaolin) soil samples using a broad spectrum of extractants (chelating agents and organic acids). Chen and Hong [39] reported on the chelating extraction of Pb and Cu from an authentic contaminated soil using derivatives of iminodiacetic acid and L-cysteine. Wuana et al. [40] investigated the removal of Pb and Cu from kaolin and bulk clay soils using two mineral acids (HCl and H₂SO₄) and chelating agents (EDTA and oxalic acid). The use of chelating organic acids—citric acid, tartaric acid and EDTA in the simultaneous removal of Ni, Cu, Zn, Cd, and Pb from an experimentally contaminated sandy loam was carried out by Wuana and his coworkers [41].

Removal of copper and nickel by the addition of the biodegradable chelating agent, chitosan and ethylenediamine tetraacetic acid (EDTA), alongside the reaction of a reference compound sodium citrate for comparison, was investigated, by Wei Jiang et al. The experiments showed that the extraction ability for copper and nickel from the contaminated soil decreased as follows: chitosan > EDTA > sodium citrate [42].

3. Conclusions

Based on the experimental results, it was shown that the extract efficiency of heavy metals from a contaminated soil using a common organic chelating or complex forming organic compounds including chitosan, EDTA, sodium citrate, citric acid, tartaric acid, etc has been done by so many scientists. This method is found to be efficient, cost effective and with much less damaging side effects than most of the methods used for removal of heavy metals from contaminated soil.

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